



## Flow-reactor experiments and theory shed light on CVD chemistry

Multilayer thin films are commonly used to improve the energy efficiency of architectural glass, also known as "float" glass.\* Thin-film materials of interest include tin oxide, indium-doped tin oxide, and titanium nitride. Although sputtering techniques have traditionally been used to deposit these films, chemical vapor deposition (CVD) methods are also in use and are becoming more attractive because coatings can be applied directly to the glass while it is on the float line. However, achieving an optically uniform coating is a particularly challenging problem, since the glass is nearly 4 m wide and is moving at ~30 cm/s.


Understanding the chemical reactions that the film precursors undergo during deposition is a particularly important aspect of process development, since their kinetics can affect issues such as long-term storage, transport through heated lines, deposition rate, and byproduct formation. Knowledge of these reactions is also essential to the development of process models for predicting film growth. Unfortunately, little is known about this chemistry. Mark Allendorf, Carl Melius, Tony McDaniel, and Scott Ferko are working with Richard McCurdy at Libbey-Owens-Ford Co. (LOF) to develop a deeper understanding of the chemistry of indium-containing precursors used by LOF to deposit indium tin oxide. The work is funded through a CRADA with LOF and the DOE/Office of Industrial Technologies Glass Industry of the Future Team.

One compound that can be used to deposit indium is trimethylindium ( $\text{In}(\text{CH}_3)_3$  or TMI). Decomposition of TMI had been thought to proceed via sequential loss of methyl radicals through gas-phase reactions; early work using

flow reactors suggested an energy for loss of the first  $\text{CH}_3$  group of 42 to 47 kcal mol<sup>-1</sup>. Theoretical and experimental investigations by Mark and his colleagues now suggest that this bond is actually much stronger and that most, if not all, previous experimental observations can be accounted for by reactions on flow-reactor walls and not in the gas-phase.

The evidence for this is based first on *ab initio* quantum chemistry calculations. Although basis sets are not available for indium, trends in predicted M-CH<sub>3</sub> bond energies (M = B, Al, or Ga) suggest that the In-CH<sub>3</sub> bond should be greater than 65 kcal mol<sup>-1</sup> (see Fig. 1).

In addition, experiments conducted in a high-temperature flow reactor equipped with a molecular-beam mass spectrometer show that decomposition of TMI involves reactions occurring on the reactor walls. The initially clean tube walls become coated over a period of minutes with an indium-containing compound, possibly  $\text{InCH}_3$ , which may form when TMI contacts the hot surface and releases hydrocarbons to the gas-phase. During the initiation period, the TMI loss rate is slow and is inconsistent with a bond energy of ~45 kcal mol<sup>-1</sup>. Subsequently, however, the reactor walls become catalytically activated and the decomposition of TMI accelerates markedly. In helium carrier gas, ethane is now produced and an activation energy for the decomposition more consistent with literature values is observed (see Fig. 2).

The results of these investigations indicate that a thorough reexamination of some of the accepted values of organometallic bond energies for Group III compounds may be necessary. In addition to TMI, the thermochemistry of trimethylaluminum and trimethylgallium may also be in error. Ongoing investigations are attempting to resolve these questions. 

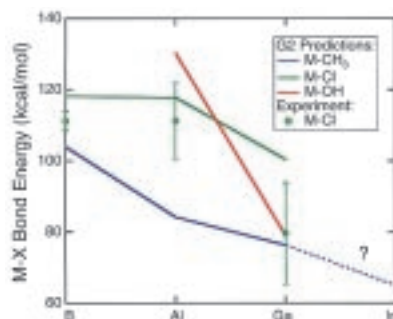


Fig. 1. Predicted energies for dissociation of the first M-X bond for compounds of the type  $\text{MX}_3$ . The results for  $\text{M}(\text{CH}_3)_3$  compounds suggest that the strength of the In-C bond in  $\text{In}(\text{CH}_3)_3$  is at least 65 kcal mol<sup>-1</sup>. An estimate of the accuracy of the calculations is exhibited by the green circles w/ error bars, which represent literature values (with uncertainties) for  $\text{MCl}_3$  compounds.

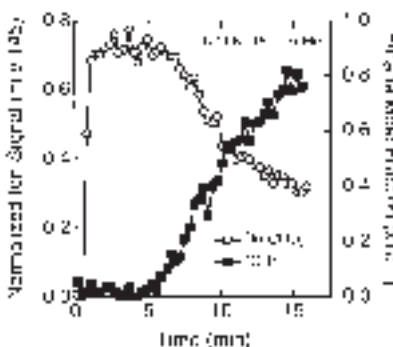


Fig. 2. Time evolution of mass-spectrometer signals corresponding to TMI ( $m/e$  145) and ethane. At time 0.5 min, a flow of TMI is initiated. At times up to 6 min, TMI appears to be stable at 673 K. At longer times, however, the TMI concentration begins to drop and substantial amounts of ethane are produced.

\*Glass produced by floating a layer of molten glass on a bath of molten tin in order to control its thickness



Allen Robinson (left) and Steve Buckley (right) recently completed post-doctoral appointments working with Larry Baxter. Allen, whose research was principally on *in situ* characterization of porous media properties and biomass-coal cofiring, has accepted a faculty position at Carnegie Mellon University. Steve, who worked primarily on energetic materials combustion, fate of radionuclide contaminants in biomass during combustion, and tunable diode laser diagnostics, is now working with the Center for Exploratory Systems and Development at Sandia/California.



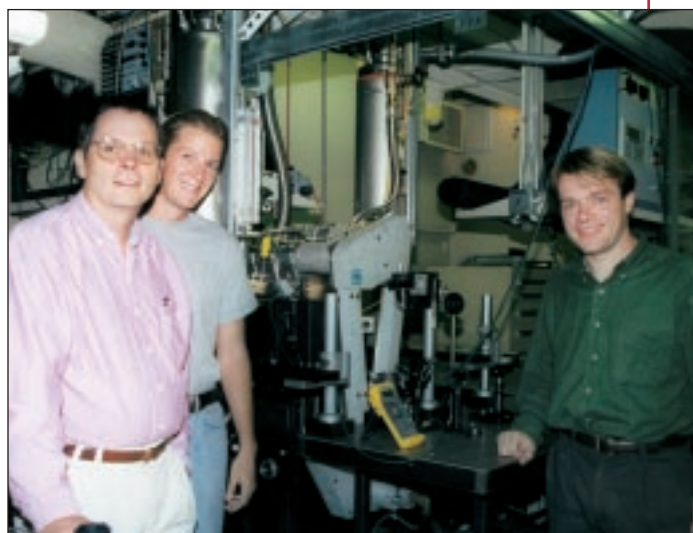
Christophe Raffy (center) of Institut National Polytechnique Grenoble, France, spent six months with Jim Miller (left) and Mark Allendorf (right) working on solving the master equation for the low-pressure-limit unimolecular dissociation of some small molecules.



Youssef Marzouk (seated) of the Mechanical Engineering Department, MIT, conducted research during August on unsteady flames with Habib Najm (standing).



Jacqueline Chen was honored by being one of the 83 young engineers selected for the National Academy of Engineering's fourth annual Frontiers of Engineering Symposium, held in September in Irvine, CA. Jackie was chosen from among more than 240 candidates to attend this peer collaboration. The symposium featured topics such as advanced materials, robotics, simulation in manufacturing, and optical imaging. Former Secretary of Defense William J. Perry was one of the keynote speakers.



Darin Knaus (center), a visiting researcher from Cornell University, has completed a study related to turbulent reaction rates in spark ignition engines with Paul Miles (left) and Pete Hinze (right). Darin's research involved determination of the orientation of the flamelet surface normal using a crossed-plane imaging technique.

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# Ignition improvement of diesel sprays studied

Brian Higgins, Dennis Siebers, and Chuck Mueller, in collaboration with Allen Aradi of Ethyl Corporation, have been investigating the effects of 2-ethylhexyl nitrate (an ignition-promoting fuel additive) on diesel spray processes. The experiments were conducted in an optically-accessible combustion vessel that simulates conditions in a direct-injection diesel engine.

The additive effects were explored by comparing results for three fuels. The first had a cetane number (CN) of 45 (a measure of ignition quality). The second fuel was blended to have a higher ignition quality, a CN of 55. The third fuel was made by adding 2-ethylhexyl nitrate to the CN 45 fuel to generate a second CN 55 fuel.

The primary effect of the fuel additive was found to be an acceleration of the preignition radical-pool formation,

leading to a shorter ignition period. No effects of the additive on other aspects of the diesel spray, such as flame lift-off, fuel vaporization, and spray dispersion were found.

Figure 1 presents a sequence of images showing the spatially-resolved evolution of luminosity during the ignition of a typical diesel spray. The lighter gray regions in the images are the result of chemiluminescence from excited state species in the radical pool. The chemiluminescence region grows spatially and in intensity with time. The very bright spots in the later images are from soot incandescence and occur after significant heat release has begun. The images show that ignition occurs over a spatially broad region of the spray.

The effects of the additive on ignition are illustrated in Fig. 2, which compares the spatially-averaged evolution of the early chemiluminescence and the ensuing soot incandescence for the three fuels. The initial rise in signal in the lower half of the figure (below the horizontal bar) results from both spatial and temporal growth in the preignition radical-pool chemiluminescence shown in the images in Fig. 1. The sudden rise in luminosity that begins within the horizontal bar is from soot incandescence that occurs after the start of significant combustion.

Comparison of the three fuels in Fig. 2 shows that the development of the radical pool for additized CN 55 fuel is very similar to the unadditized CN 45 “parent” fuel, except that it is shifted earlier in time.

These observations support the arguments that 2-ethylhexyl nitrate decomposes very early in the spray development and

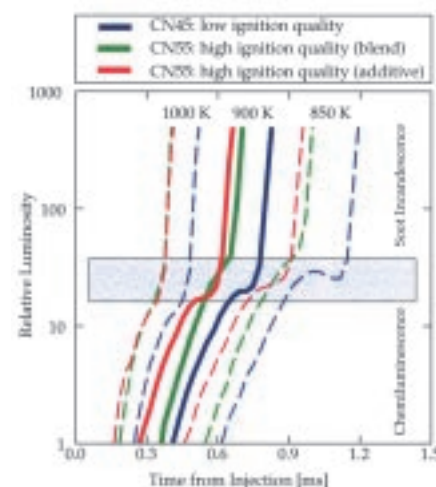


Figure 2. Relative luminosity traces at 430 nm at an ambient gas density condition of 14.8 kg/m<sup>3</sup> for three ambient gas temperatures for each fuel.

enhances the earliest phases of the radical pool formation leading up to ignition. The later stages of the radical pool formation are controlled by the major constituents of the unadditized “parent” fuel.

The results suggest that the effects of the additive on engine performance and emissions are the result of changes in the timing of the diesel combustion event relative to the engine cycle, and are not the result of fundamental changes in diesel combustion process beyond the changes in the earliest stages of the ignition process.

This research was funded by Ethyl Corporation. 

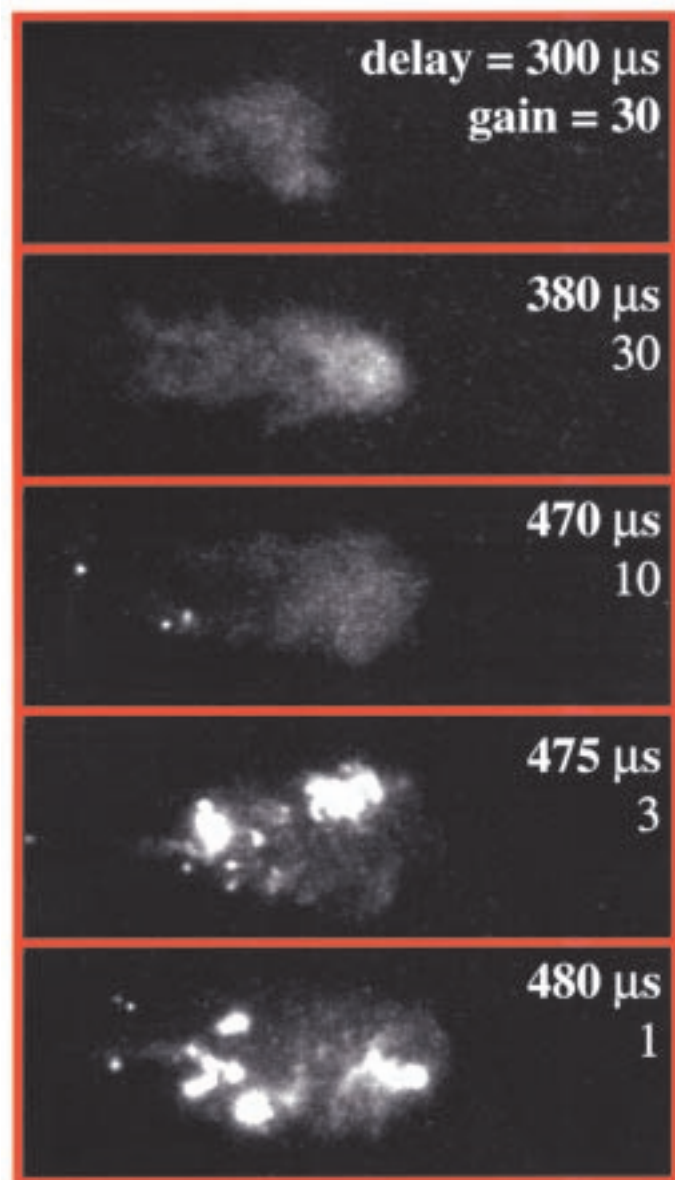


Figure 1. A time sequence of images of chemiluminescence (lighter gray regions) and soot incandescence (bright spots) during ignition taken with an intensified CCD camera. The fuel is injected from left to right in each image. Given in each image is the time after the start of injection (delay) and the camera gain relative to the bottom image.

# Rotational energy transfer investigated in new picosecond spectroscopy lab


Accurate measurements of rotational energy transfer (RET) rates are essential for quantitative application of laser-based spectroscopic diagnostic methods, such as absorption spectroscopy and laser-induced fluorescence (LIF). To date, most experimental RET studies have been performed using stable molecules and/or molecules prepared in an electronically excited state. Dahv Kliner and Roger Farrow have now measured ground-state RET rates for the OH radical, a key oxidant in flames. These measurements were performed in the new picosecond spectroscopy laboratory, which was established as part of the CRF Phase II development, with the assistance of Perry Yaney (University of Dayton) and Paul Schrader.

LIF detection of OH is widely used in a variety of applications, including laboratory studies, combustion measurements, and atmospheric sensing. For applications in which the temperature or composition are variable, knowledge of OH RET rates is required for accurate determination of OH densities and for OH thermometry. RET is particularly important for determining the line shapes and saturation behavior of OH.

Dahv and Roger generated rotationally hot ( $\sim 1700$  K) OH in the ground electronic and vibrational states by photolyzing  $\text{H}_2\text{O}_2$  with a 266-nm laser pulse. Collisional

relaxation of the OH by a bath gas ( $\text{N}_2$ ,  $\text{O}_2$ ,  $\text{H}_2\text{O}$ , or Ar) was monitored by recording LIF spectra using a second, variably delayed laser pulse at  $\sim 282$  nm. The duration of each laser pulse was  $\sim 100$  ps, allowing the time evolution of the OH rotational distribution to be followed with high temporal and spectral resolution. Figure 1 shows a representative LIF spectrum.

The time evolution of the OH rotational distribution for the bath gas  $\text{N}_2$  is shown in Fig. 2. At intermediate times, the distribution is “kinked”, indicating more efficient RET for low  $N''$  than high  $N''$ . The bath gases  $\text{O}_2$  and Ar behaved similarly, but  $\text{H}_2\text{O}$  did not show such a pronounced dependence of RET rate on  $N''$ . Moreover, the RET rate for  $\text{H}_2\text{O}$  was approximately an order of magnitude faster than for the other bath gases.

To extract RET rate constants from the observed time evolution of the OH rotational distribution, the data were fit using various models for the state-to-state RET rate matrix. An exponential-gap model (lines in Fig. 2) is remarkably successful in reproducing the measured distributions for all four bath gases. These rates may be incorporated into spectroscopic models used to extract OH quantum-state population distributions from measured LIF spectra. 

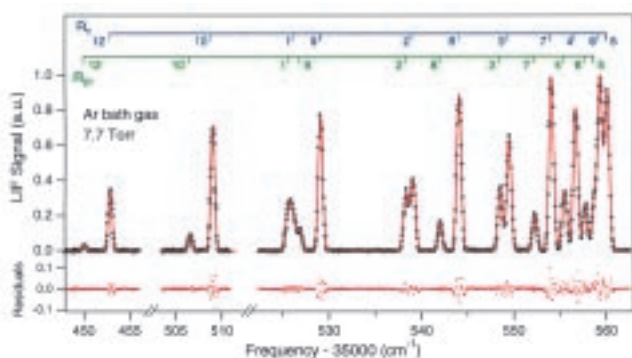


Fig. 1. OH LIF spectrum (points) and the least-squares fit (line) from which the rotational population distribution was derived. Line assignments (branch and rotational quantum number,  $N''$ ) are given above the spectrum.

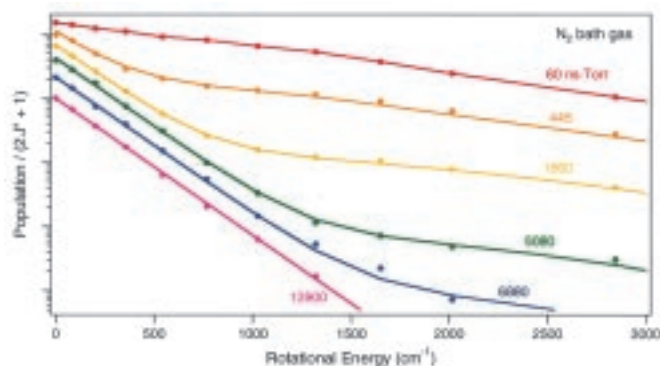


Fig. 2. Boltzmann plots of the OH rotational distribution at the indicated pressure-time products following photolysis. The points are the experimental data; the lines are the corresponding distributions from the best-fit exponential-gap model. Data at the different times have been offset for clarity.

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